

Anal. Calcd. for $C_{17}H_{17}O_6N_5$: C, 52.72; H, 4.39; N, 18.10. Found: C, 52.66; H, 4.43; N, 18.22.

This same product VII could be obtained in very low yield when ethyl cyanoacetate was treated with two molar equivalents of acrolein under similar reaction conditions.

The low pressure reduction of compound VII to 1-formyl-5-carbethoxy-5-cyanocyclohexane (VIII) proceeded

smoothly in the presence of 5% palladium-on-charcoal when the previously described conditions were employed. Compound VIII was also identified as the 2,4-dinitrophenyl-hydrazone which melted at 125–126°.

Anal. Calcd. for $C_{17}H_{19}O_6N_5$: C, 52.44; H, 4.88; N, 17.99. Found: C, 52.30; H, 5.06; N, 18.23.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polyalkylene Sulfides. V. The Rate of Formation in Emulsion¹

BY C. S. MARVEL AND A. H. MARKHART, JR.²

The rate of disappearance of mercaptan groups in the emulsion polymerization of diolefins and dimercaptans has been found to be very rapid; approximately 90% in 5 minutes. However, many hours are required for the polymer to attain its maximum molecular weight.

Previous papers of this series^{3–6} have described the preparation and properties of a number of polymers obtained by the reaction of diolefins and dimercaptans. In order to determine the conditions for the formation of higher molecular weight products, it appeared advisable to follow the reaction quantitatively. This paper presents the results of a study of the over-all rate of the reaction between diolefins and dimercaptans in a redox-activated emulsion system.

Experimental

The reaction was followed in two ways: first, by determining the rate of disappearance of mercaptan from the emulsion and, secondly, by the rate of growth of polymer molecules as determined by inherent viscosity measurements.

Rate of Mercaptan Disappearance.—An emulsion of hexamethylenedithiol was prepared by tumbling overnight in a nitrogen atmosphere 1.39 g. of this compound in 60 ml. of a 1% solution of MP-189-EF⁷ buffered at pH 3.5. An aliquot of this emulsion was analyzed for thiol by the Kolthoff-Harris⁸ amperometric titration procedure described below. Fifty milliliters of this emulsion was transferred to a 4-oz., nitrogen-filled wide-mouth screw-cap bottle. One milliliter of activator solution was added and a small vial (16 × 25 mm.) containing an equivalent quantity of diolefin dropped in. The bottle was immediately capped and shaken. At various time intervals, the bottle was opened and a slow stream of nitrogen introduced while an aliquot was removed by pipet for analysis. Due to the short time intervals between sampling during the first part of the reaction, the bottle was shaken by hand in air for the first 15 minutes; the remainder of the run was carried out by tumbling in a 30° bath. An alternative sampling technique employing a hypodermic syringe and bottles fitted with self-sealing liners was found to give less accurate aliquots, and in the case of certain thiols, severe attack of the liners was encountered. The persulfate catalyst itself was found to have but a very slight effect upon the determination of the mercaptan concentration.

Rate of Polymer Growth.—The polymerization was carried out in essentially the same manner as described above

but with four times as much material. At the specified time intervals 10-ml. aliquots of the emulsion were removed by pipet and coagulated with an alum-hydrochloric acid solution. The coagulated polymer was collected by filtration, washed with water and methanol and air-dried. The dry powder was dissolved in 15 ml. of chloroform, the solution filtered and poured slowly into 150 ml. of methanol. The samples were collected and dried in a vacuum desiccator prior to viscosity determination.

Inherent Viscosity Determinations.—Polymer samples (0.200 g.) were dissolved in 50 ml. of chloroform and the viscosity of these solutions measured in an Ostwald-Fenske type viscometer at 25.0°.⁹

Monomers.—Biallyl (1,5-hexadiene), dimethylbiallyl (2,5-dimethyl-1,5-hexadiene) and hexamethylenedithiol were prepared by standard procedures.⁵ Ethanedithiol and bis-(2-mercaptoethyl) sulfide were gifts from the Thiokol Corporation. All monomers were redistilled before use.

Amperometric Titrations.—The procedure followed was that of Kolthoff and Harris⁸ in which the mercaptan is titrated with silver nitrate using a rotating platinum wire electrode. The titrations were carried out in ammoniacal solution prepared as follows: 100 ml. of 95% ethanol was placed in a 250-ml. beaker. Approximately 0.4 g. of ammonium nitrate was dissolved in the alcohol and 1.7 ml. of concentrated ammonium hydroxide added. The mercaptan sample was then placed in this solution and titrated with 0.005 *N* silver nitrate. The points obtained near the end-point did not lie on the straight line of the volume of reagent versus current graph. The points obtained at currents above 10 microamperes were in general very reliable and found to lie on a straight line.

Activator.—A solution of 2.150 g. of ammonium persulfate, 1.108 g. of sodium bisulfite and 0.110 g. of cupric sulfate pentahydrate was prepared from reagent grade materials and diluted to 100 ml. Aliquots of this solution were employed as activators, 1 ml. per 50 ml. of emulsion. The solutions were made up within 5 minutes of each run.

Results and Discussion

The data for the rate of disappearance of mercaptan in the reactions of hexamethylenedithiol with biallyl and dimethylbiallyl are given in Table I and Fig. 1.

The great speed of this type of reaction is clearly shown. Visual evidence of the rapidity of the polymerization is given by the fact that even a 45-second sample, when injected into ethanol for titration, precipitated a product already insoluble in alcohol. Also, within the first few minutes of reaction the emulsion changes from a milky-white opaque mixture to an opalescent, semi-transparent latex. This is indicative of the disappearance of monomer droplets and the formation of polymer-

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the U. S. Government Synthetic Rubber Program.

(2) Research Department, Monsanto Chemical Company, Everett, Massachusetts.

(3) C. S. Marvel and R. R. Chambers, *THIS JOURNAL*, **70**, 993 (1948).

(4) C. S. Marvel and P. H. Aldrich, *ibid.*, **72**, 1978 (1950).

(5) C. S. Marvel and H. E. Baumgarten, *J. Pol. Sci.*, in press.

(6) C. S. Marvel and G. Nowlin, *THIS JOURNAL*, **72**, 5026 (1950).

(7) MP-189-EF is an electrolyte free emulsifier which consists essentially of mixed alkanesulfonic acids. We are indebted to Dr. Stanley Detrich of Jackson Laboratory, E. I. du Pont de Nemours and Company, for this material.

(8) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

(9) L. C. Cragg, *J. Coll. Sci.*, **1**, 261 (1946).

TABLE I
RATE OF DISAPPEARANCE OF MERCAPTAN IN REACTION WITH
DIOLEFINS IN EMULSION (30°)

| Time, min. | Ml. 0.005 N AgNO ₃ Equivalent to 1 ml. emulsion | | Mercaptan Biallyl | Mercaptan reacted, % Dimethyl- biallyl |
|---------------|---|----------------------|----------------------|---|
| | Biallyl | Dimethyl- biallyl | | |
| 0 | 77.80 | 56.80 | .. | |
| 2 | 23.81 | 11.50 | 68.8 | 79.7 |
| 4.5 | 6.50 | | 91.5 | |
| 5 | | 7.11 | | 87.4 |
| 8.5 | 3.35 | | 95.6 | |
| 9 | | 5.98 | | 89.5 |
| 16 | 1.20 | 5.85 | 98.4 | 89.8 |
| 45 | 1.05 | | 98.6 | |
| 1 hr. | 0.83 | 5.22 | 98.9 | 90.9 |
| 2 days | 0.10 | .. | 99.9 | .. |

monomer micelles. During the first part of the reaction a noticeable temperature increase can be detected. When the reaction was carried out with a 10% excess of biallyl, the disappearance of thiol was found to be 96.2% complete after five minutes and 99.8% complete after two hours.

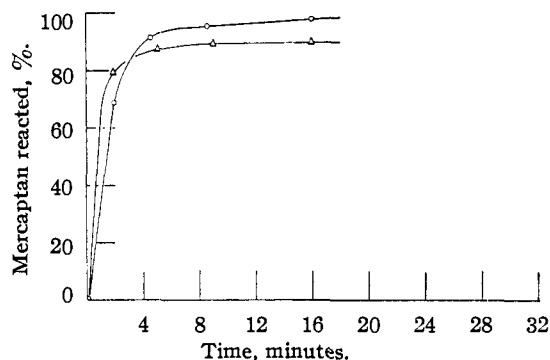


Fig. 1.—The rate of disappearance of mercaptan by reaction with biallyl and dimethylbiallyl: O, biallyl; Δ, dimethylbiallyl.

A similar study was made of the reaction between biallyl and ethanedithiol. The rate of the reaction in this case was only slightly less than that with hexamethylenedithiol, 85.2% of the thiol disappearing within six minutes. This result was interesting because the polymers that have been prepared from ethanedithiol and biallyl have possessed lower molecular weights than the corresponding products from hexamethylenedithiol. Another dithiol, bis-(2-mercaptoethyl) sulfide, behaves in essentially the same manner as ethanedithiol.

In view of the high rate of disappearance of mercaptan in the polymerizations studied above, it was of interest to compare the rate of growth of the polymer molecules with the rate of reaction of the mercaptan groups. The rate of growth of the polymer molecules as indicated by inherent viscosity measurements is shown in Table II and Fig. 2.

TABLE II
RATE OF GROWTH OF POLYHEXAMETHYLENE SULFIDE
MOLECULES (30°)

| Time | Inherent viscosity | Time | Inherent viscosity |
|--------|-----------------------|--------|-----------------------|
| 5 min. | 0.608 | 18 | 1.091 |
| 30 | .738 | 2 days | 1.074 |
| 1 hr. | .824 | 3 | 0.982 |
| 2 | .907 | 9 | 0.998 |

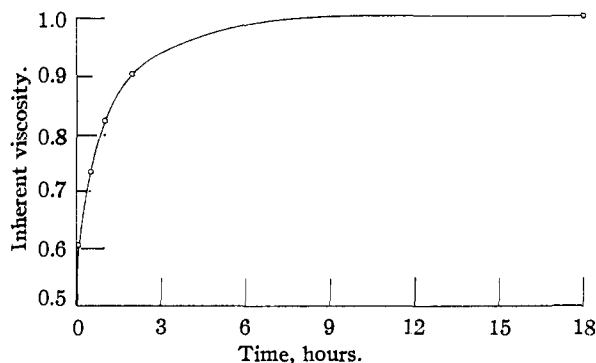
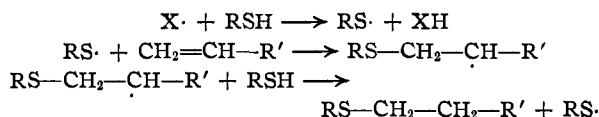


Fig. 2.—The rate of growth of polymer molecules in the reaction of biallyl and hexamethylenedithiol.

The maximum inherent viscosity had been reached in 18 hours. A similar experiment with dimethylbiallyl and hexamethylenedithiol had shown that 48 hours was required for the maximum molecular weight to be reached with that monomer pair.⁵ Comparison of Figs. 1 and 2 shows plainly how the growth of the polymer molecules lags behind the rate of reaction of the mercaptan groups.

This type of reaction is thus unique in that it combines features of both a chain-propagated, free radical polymerization and a condensation polymerization. The latter type possesses the characteristic of polymer molecules increasing in size at a progressively slower rate such as is shown by the reaction described above. Although no truly kinetic study of this reaction has been carried out, the mechanism probably involves the attack of an activator free radical upon the mercaptan to produce RS· radicals. These can then react with olefinic double bonds to form RS-CH₂-CH-R' units which can then start another cycle by extracting a hydrogen atom from another thiol group. This may be summarized



Chain-terminating reactions may occur by combination of the radicals produced in the reaction sequence outlined above. Such reactions may be significant in limiting the maximum molecular weight of the polymer molecules which are formed, but that they do not occur to any great extent is indicated by the fact that high yields of analytically pure polyalkylene sulfides are obtained. It appears that during the first part of the polymerization the monomers react rapidly to form large numbers of relatively small molecules and that as the reaction proceeds, increasing numbers of these larger units react with other units which possess opposite end groups. This latter type of reaction, however, is relatively slow due to the difficulty which the terminal groups have in finding the appropriate terminal group or radical with which to react in this two-phase system. This at least qualitatively explains the rapid initial disappearance of thiol groups and the relatively slow increase in average molecular weight at the end of the reaction.